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Simultaneous removal of multiple heavy metals from soil by washing with citric acid and ferric chloride†

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The remediation of soil contaminated with multiple heavy metals is a matter of great concern due to its serious threat to the ecosystem and human health. Batch and slurry reactor soil washing experiments were conducted to explore the removal of Cd, Cr, Pb and Zn using 7 agents. Citric acid (CA) and ferric chloride ($FeCl_3$) exhibited an obvious synergistic effect on the removal of heavy metals. Furthermore, the concentration of heavy metals in different soil particle size fractions was closely related to the soil element concentrations. Fine sand (0.05–0.25 mm) had a strong adsorption capacity for Cr and Pb because of the high Mn concentration. Notably, heavy metals in smaller-size soil particles could be efficiently removed by CA and $FeCl_3$. After remediation, the bioavailability of heavy metals in soil decreased. The potential ecological risk of heavy metals in soil reduced from an extremely high level to a low level. Moreover, some elements (*e.g.* Al, Mn and Fe) and organic matter in soil were dissolved by CA and $FeCl_3$, which accelerated the desorption of heavy metals from the soil. In a slurry reactor experiment, the removal efficiencies of Cd, Cr, Pb and Zn were 94.8%, 79.5%, 92.7% and 97.2%, respectively. The combination of CA and $FeCl_3$ is a feasible practice to remediate soil contaminated by multiple heavy metals.

1. Introduction

Soil contamination with heavy metals is one of the important environmental problems in the world. It is mainly derived from anthropogenic activities, including mining, electroplating, metallurgy and other industries.[1,2] Multiple heavy metals (including Cd, Cr, Pb, Zn and Hg)[3,4] represent a threat to the environment and human health due to their persistence in soil and potential uptake by crops.[5] Therefore, the remediation of soil contaminated by heavy metals, particularly in combination with different pollutants, is of practical significance.[6] Various techniques, including physical methods (soil replacement, thermal treatment), chemical methods (solidification/stabilization, soil washing) and biological methods (microbial remediation, phytoremediation) have been conducted for solving this environmental issue.[7–11] Soil washing offers great advantages in soil remediation for its simple operation and permanent removal of heavy metals from soil.[7,12]

Various agents, including acids, bases, chelating agents, surfactants and other additives, have been employed to remove heavy metals from soil.[13–15] Although acids could increase the solubility of metals, strong acids may destroy the soil structure, which is unsuitable for revegetation.[16] Consequently, synthetic chelates, such as ethylenediamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA), have been used for soil remediation because of their strong chelating ability for different heavy metals.[17] However, they have poor biodegradability and are unstable at high temperatures.[18] In recent years, citric acid (CA), a tricarboxylic acid compound, has played an important role in removing heavy metals from soil *via* acid dissolution and chelation,[19] and is more readily biodegradable than EDTA.[20,21] Notably, CA leaches lower contaminants (*e.g.* Cd and Ni) than EDTA, except for Cr.[22,23] Salt and chloride solutions (*e.g.* $CaCl_2$ and $FeCl_3$) are also promising washing agents, which have been verified to decrease heavy metal content, especially that of Cd, in soil and crops.[24–26] $FeCl_3$ can remove Cd through proton release and formation of soluble complexes with Cd.[27] Different washing agents show affinity and selectivity for different heavy metals in soil. Studies have shown that the removal efficiencies of multiple heavy metals can be significantly improved by composite washing. The combination of ferric nitrate and EDDS was useful for the removal of Pb and Cu from

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soil.[28] Combining washing reagents dramatically enhanced the removal efficiencies of Pb and Zn by using Na_2EDTA and either tartaric acid or lactate.[21] Hence, searching for efficient and environmentally friendly composite washing agents is a critical step for the remediation of co-contaminated soil.[29]

Batch and slurry reactor washing experiments were conducted to explore the removal of Cd, Cr, Pb and Zn from contaminated soil using 7 agents. The objectives of this study were as follows: (1) select efficient agents for soil remediation; (2) obtain the optimal conditions of washing with CA and $FeCl_3$; (3) explore the concentrations and removal efficiencies of heavy metals in different soil particle-size fractions; (4) assess the pollution level and potential ecological risk of heavy metals in soil before and after remediation.

2. Materials and methods

2.1. Soil characteristics

Soil samples were collected from a demolished industrial site in Hangzhou City, Zhejiang Province, China. Samples were air-dried at room temperature, then ground and passed through a 2 mm sieve for analysis. The concentrations of Cd, Cr, Pb and Zn in the soil were determined by flame atomic absorption spectroscopy (FAAS, MKILM6) after triacid digestion (HNO_3–HF–$HClO_4$). The Cr(VI) concentration in soil was determined by the diphenylcarbazide spectrophotometric method[30] after extraction with Na_2CO_3 and NaOH. The concentrations of Cd, Cr, Cr(VI), Pb and Zn were 646.7, 4802.0, 272.9, 9587.0 and 20 079.0 mg kg^{-1}, respectively. The soil was neutral (pH 7.0 ± 0.1), the organic matter content was 8.7 ± 0.3% and the cation exchange capacity (CEC) of the soil was 14.5 ± 0.3 cmol kg^{-1}. The soil was classified as sandy loam according to the USDA soil classification (6.8% clay, 33.6% silt and 59.6% sand).

2.2. Selection of promising agents for soil washing

In order to select efficient composite washing agents, the removal of heavy metals by washing with 7 agents (citric acid (CA), oxalic acid (OA), phosphoric acid (H_3PO_4), nitric acid (HNO_3), ferrous chloride ($FeCl_2$), ferric chloride ($FeCl_3$) and disodium ethylenediaminetetraacetic acid (Na_2EDTA)) was explored respectively in this study. The washing solution concentrations were 0.1, 0.5 and 1.0 mol L^{-1}, respectively (washing time of 10 h, liquid : soil ratio of 10 : 1). Subsequently, CA, OA, HNO_3, and $FeCl_3$ (0.5 mol L^{-1}) were combined in pairs for composite washing because of their relatively high removal efficiency. The volume ratios of agents were 8 : 2, 5 : 5 and 2 : 8, respectively. Each group was carried out at least in triplicate.

2.3. Determination of optimum washing conditions

Batch experiments were set to obtain the optimum washing conditions of CA and $FeCl_3$ (v/v, 5 : 5). The explored washing solution concentrations were 0.25, 0.5, 0.75 and 1.0 mol L^{-1}, respectively. Each group was carried out at least in triplicate. The optimum concentrations of agents would be used for further experiments. In addition, the optimum washing time and liquid : soil ratio were also investigated, with detailed experimental setups described in the ESI.†

Soil samples and washing agents were added into 50 mL centrifuge tubes, and mixed under 180 rpm at 25 °C. After washing, the tubes were centrifuged for 10 min at 5000*g*, and the supernatant was then filtered through a 0.45 μm membrane. The concentrations of Cd, Cr, Pb and Zn were determined by flame atomic absorption spectroscopy (FAAS, MKILM6).

2.4. Composite washing combined with sieving pretreatment

Silty clay (<0.05 mm), fine sand (0.05–0.25 mm) and coarse sand (0.25–2 mm) were separated by 300, 60 and 10 mesh sieves, respectively. The removal of heavy metals in different treatments was explored with a washing time of 10 h and liquid : soil ratio of 10 : 1. Each group was carried out at least in triplicate. The other experimental steps were the same as Section 2.3. After washing, the soil was washed three times with deionized water and then freeze-dried for further analysis. The morphology and element distribution of soil samples were observed *via* a scanning electron microscopy (SEM, SU-8010) and an energy dispersive spectrometer (EDS, X-MaxN 80), respectively.

2.5. Sequential extraction procedure

Sequential extraction (Tessier's method)[31] was used to investigate the speciation of heavy metals in soil. In short, heavy metal species were categorized into 5 fractions: exchangeable fraction (F_1, extractable with 1 mol L^{-1} $MgCl_2$ at pH 7.0), bound to carbonates fraction (F_2, extractable with 1 mol L^{-1} NaAc–HAc at pH 5.0), bound to Fe–Mn oxides fraction (F_3, extractable with 0.04 mol L^{-1} $NH_2OH\cdot HCl$), bound to organic matter fraction (F_4, extractable with 0.02 mol L^{-1} HNO_3 and 30% H_2O_2 at pH 2.0) and residual fraction (F_5, digestible with HNO_3–HF–$HClO_4$).

2.6. Slurry reactor experiment

The polymethyl methacrylate column used in this study was of a 25 cm inner diameter and 25 cm height. The details of the slurry reactor are shown in the ESI (Fig. S1†). Contaminated soil (1 kg) and washing agents (CA and $FeCl_3$, optimal washing conditions) were added into the reactor. The stirring speed was 180 rpm, and the temperature was 25 °C. The sampling intervals and other experimental steps were the same as Section 2.3. After washing, the soil was washed three times with deionized water and then freeze-dried for analysis. Molecular spectra of soil were recorded in the 4000–400 cm^{-1} region on a Fourier transform infrared spectrometer (FTIR, AVATAR370).

2.7. Statistical analysis

The Cd, Cr, Pb and Zn concentration data were reported as the mean value ± standard deviation (SD) of at least three replicates for each treatment. One-way ANOVA was performed to assess the statistical significance ($P < 0.05$) between different treated groups by SPSS 20.0.[32] The response surface methodology (RSM) based central composite design (CCD) was used to establish the response surface maps and the optimum agent concentrations by Design Expert 8.0.[33]

3. Results and discussion

3.1. Selection of washing agents

The selection of efficient washing agents is the key to co-contaminated soil remediation. The removal of Cd, Cr, Pb and Zn from soil by 7 washing agents was investigated in this study. The removal of heavy metals was positively related to the agent concentration, except for Na_2EDTA (Fig. S2†). The removal efficiencies of heavy metal washing by 7 agents were as follows (agent concentration of 0.5 mol L^{-1}): for Cd, $FeCl_3 \approx$ CA $\approx HNO_3 > H_3PO_4 > Na_2EDTA \approx FeCl_2 >$ OA; for Cr, OA > CA > $HNO_3 > H_3PO_4 > FeCl_3 > Na_2EDTA > FeCl_2$; for Pb, $FeCl_3 \approx Na_2EDTA > FeCl_2 >$ CA > $HNO_3 \approx$ OA $\approx H_3PO_4$; for Zn, $FeCl_3 \approx HNO_3 \approx$ CA $\approx H_3PO_4 > FeCl_2 > Na_2EDTA >$ OA. $FeCl_3$, CA, HNO_3 and H_3PO_4 were efficient agents for the removal of Cd and Zn, and OA and CA were efficient agents for the removal of Cr from soil.

Notably, $FeCl_3$ exhibited a high extraction efficiency for Cd, Pb and Zn (Table S1†). The removal efficiencies of Cd, Cr, Pb and Zn were 67.7%, 15.6%, 98.2% and 69.4%, respectively. Studies have shown that the hydrolysis of $FeCl_3$ results in the release of protons and the synthesis of hydroxides.[34] Furthermore, the stable and soluble metal chloro-complexes were formed with Cl^- in the solution, which prevented heavy metals from being re-absorbed into the soil.[12] Similarly, $FeCl_3$ has also proven to be the most stable washing agent for Pb removal, and is cheap and easy to handle.[25,35] In addition, CA exhibited a high extraction efficiency for heavy metals, especially Cr. The removal efficiencies of Cd, Cr, Pb and Zn were 78.4%, 44.4%, 51.5% and 81.2%, respectively. Furthermore, CA has been considered to be the best for the remediation of Cr(VI) contaminated wastes and soils,[22,36] and was more biodegradable and less toxic.[37]

Finally, the combination of CA and $FeCl_3$ (5 : 5, v/v) was chosen for simultaneously removing multiple heavy metals from soil. The removal efficiencies of Cd, Cr, Pb and Zn (Table S1†) were 73.1%, 41.3%, 98.0% and 71.4%, respectively.

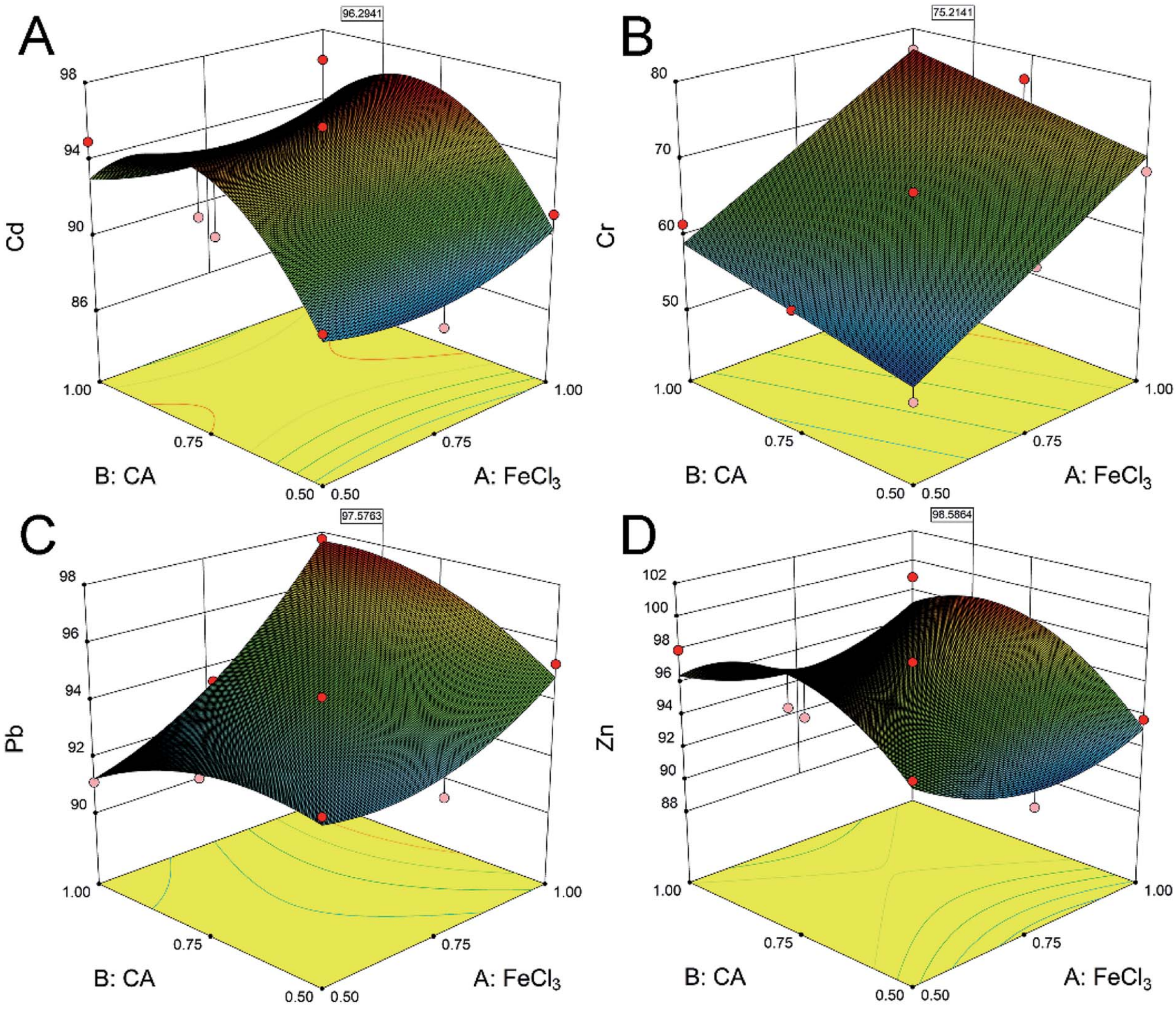

Fig. 1 Response surface maps of the effects of different CA and $FeCl_3$ concentrations on the removal efficiencies of Cd (A), Cr (B), Pb (C) and Zn (D) in contaminated soil.

3.2. Optimization of composite washing conditions

To determine the optimum washing conditions, the effects of agent concentration, washing time and liquid : soil ratio on the removal of heavy metals were investigated in this study. Generally, the removal of heavy metals is positively related to the concentration of the agent.[38] Differently, there was an obvious quadratic parabolic correlation between the CA concentration and the removal efficiencies of Cd and Zn (Fig. 1A and D). The removal efficiencies of Cd were 87.9%, 95.7% and 87.4%, and the removal efficiencies of Zn were 91.6%, 97.3% and 91.0%, at the $FeCl_3$ concentration of 0.75 mol L^{-1} and CA concentrations of 0.50, 0.75 and 1.00 mol L^{-1}, respectively. It was illustrated that a high agent concentration may not be conducive to the ion exchange of Cd and Zn.[39] In addition, the removal of Cr and Pb (Fig. 1B and C) was positively related to the concentrations of CA and $FeCl_3$. The removal efficiencies of Cr and Pb were respectively 77.0% and 97.7% at the CA and $FeCl_3$ concentrations of 1.00 mol L^{-1}. CA and $FeCl_3$ exhibited an obvious synergistic effect on the removal of heavy metals from soil. Subsequently, the response surface analysis[40] determined that the optimum concentrations of CA and $FeCl_3$ were 0.86 and 1.00 mol L^{-1} (Fig. S3†), respectively. The predictive removal efficiencies of Cd, Cr, Pb and Zn in the soil were 96.3%, 72.5%, 97.6% and 98.6%, respectively.

Another crucial factor is the washing time. The removal of heavy metals proceeds until a dynamic equilibrium between adsorption and desorption is reached.[32] At first, heavy metals on the soil surface were quickly desorbed into solution.[41] The removal efficiencies of heavy metals increased dramatically over time (Fig. 2A) in the early stage (<2 h). The removal efficiencies of Cd, Cr, Pb and Zn after washing for 2 h were 93.2%, 48.9%, 92.9% and 86.8%, respectively. The desorption of heavy metals became slow and reached a plateau after washing for 10 h. Notably, the removal of heavy metals was unaltered, or even decreased over time (10–24 h). Therefore, the washing time was determined to be 10 h.

The liquid : soil ratio is also an important factor affecting the desorption of heavy metals from soil.[42] A lower concentration or higher liquid : soil ratio could avoid the clogging of soil but increase costs.[43] In this study, there was no significant difference in Cd removal efficiency (94.2 ± 4.3%) under different liquid : soil ratio conditions (Fig. 2B). This indicated that Cd was more easily desorbed from soil, because Cd mostly exists as an exchangeable fraction and is very active in nature.[44] The removal of Cr, Pb and Zn was increased dramatically as the liquid : soil ratio increased from 1 : 1 to 10 : 1. The removal efficiencies of Cr, Pb and Zn reached 75.2%, 88.8% and 96.2%, respectively. Notably, the removal of heavy metals was unaltered as the liquid soil ratio increased from 10 : 1 to 30 : 1. Hence, the optimal liquid : soil ratio was determined to be 10 : 1 considering the economics of soil remediation.

3.3. Removal of heavy metals from different particle-size fractions of soil

Soils are characterized by the distribution of different soil particle-size fractions.[45] Generally, fine sand exhibits a higher affinity for heavy metals than that of coarse sand, due to its higher specific surface area and natural organic content.[16] Here, coarse sand (0.25–2 mm), fine sand (0.05–0.25 mm) and silty clay (<0.05 mm) were separated by sieving. The results (Table 1) showed that Cd and Zn were more easily accumulated in the soil of small particle-size fractions. The concentrations of Cd and Zn in silty clay were increased by 11.3% and 55.6% of those in the coarse sand, respectively. Differently, the concentrations of Cr and Pb were highest in the fine sand, which were respectively increased by 15.0% and 90.5% of those in the coarse sand.

To explore the interaction between heavy metal concentrations and the element contents of soil, the concentrations of Ca, Mg, Al, Fe and Mn in different treatments were further investigated (Table 1). The correlation analysis showed that the distributions of Cd and Zn were closely related to the Fe and Mg concentrations (Fig. S4†), followed by the concentration of Mn.

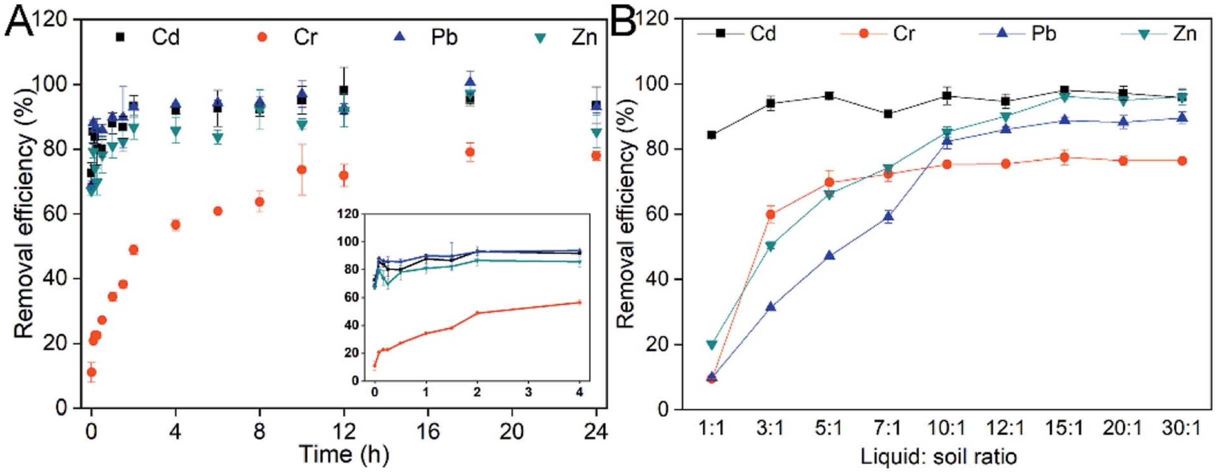

Fig. 2 Removal efficiencies of Cd, Cr, Pb and Zn in contaminated soil over time (0–24 h) by washing with CA and $FeCl_3$(A); removal efficiencies of Cd, Cr, Pb and Zn in contaminated soil at the first 4 hours (A, the inset graphic); effects of liquid : soil ratios on the removal efficiencies of heavy metals during composite washing (B).

Table 1 Concentrations of Cd, Cr, Pb, Zn, Ca, Mg, Al, Fe and Mn in different soil particle-size fractions[a]

	Concentration of metals (mg kg^{-1})			
Heavy metal	Original	Coarse sand	Fine sand	Silty clay
Cd	646.7 ± 46.0ab	629.3 ± 34.9b	665.7 ± 4.3 ab	700.6 ± 2.1a
Cr	4802 ± 161.1b	4930 ± 67.7 ab	5671 ± 46.3a	4213 ± 94.2b
Pb	9587 ± 654.9c	6884 ± 45.0d	13 115 ± 26.7a	10 625 ± 565.7b
Zn	20 079 ± 615.5b	15 508 ± 596.5d	18 967 ± 96.6c	24 137 ± 219.9a
Ca	22 007 ± 565.7bc	32 587 ± 1330.1a	22 940 ± 433.0b	21 105 ± 257.2c
Mg	3641.7 ± 85.6b	3085.8 ± 69.7d	3244.2 ± 27.7c	4559.2 ± 65.1a
Al	41 775 ± 346.4c	50 813 ± 1339.9a	39 100 ± 229.1d	45 450 ± 1039.5b
Fe	44 942 ± 1410.3b	23 046 ± 1545.5d	41 275 ± 125.0c	60 950 ± 1477.3a
Mn	63 583 ± 1418.0b	38 281 ± 1962.6c	73 258 ± 262.6a	62 550 ± 433.7b

[a] Different letters (a–d) behind the data indicate a significant difference among different particle-size fractions of soil (one-way ANOVA, $P < 0.05$).

Table 2 Removal efficiencies of Cd, Cr, Pb and Zn in different soil particle-size fractions after washing[a]

		Removal efficiency (%)			
Washing agent		Cd	Cr	Pb	Zn
FeCl$_3$	Original	95.57 ± 1.06a	23.68 ± 0.32b	96.96 ± 1.26b	89.87 ± 0.89b
	Coarse sand	99.21 ± 2.31a	19.62 ± 0.15c	70.39 ± 3.05c	96.17 ± 2.54a
	Fine sand	93.75 ± 0.36a	16.75 ± 0.38d	63.76 ± 0.83d	90.06 ± 0.27b
	Silty clay	97.09 ± 0.71a	27.13 ± 0.56a	99.64 ± 0.07a	87.19 ± 0.31b
CA	Original	94.23 ± 2.98a	68.24 ± 0.94a	42.32 ± 0.62a	95.44 ± 0.73bc
	Coarse sand	96.23 ± 2.62a	57.29 ± 2.74b	44.69 ± 1.95a	98.98 ± 2.66a
	Fine sand	92.65 ± 1.06a	46.66 ± 0.67c	24.87 ± 0.41b	98.10 ± 0.53ab
	Silty clay	95.79 ± 0.83a	68.73 ± 0.89a	42.22 ± 0.28a	93.93 ± 0.39c
CA+ FeCl$_3$	Original	94.85 ± 3.08a	75.48 ± 4.20a	91.23 ± 0.84a	94.74 ± 0.76a
	Coarse sand	93.11 ± 1.58a	74.39 ± 3.80ab	77.71 ± 1.33b	95.16 ± 2.60a
	Fine sand	93.30 ± 1.53a	65.37 ± 2.90b	68.28 ± 1.12c	92.50 ± 0.46a
	Silty clay	85.87 ± 1.87a	79.86 ± 0.72a	94.83 ± 0.70a	95.02 ± 0.73a

[a] Different letters (a–d) behind the data indicate a significant difference among different soil particle size fractions (one-way ANOVA, $P < 0.05$).

Additionally, the Pb concentration was related to the concentrations of Mn and Fe, which indicated that high contents of Fe and Mn oxides in soil could adsorb more Pb.[46] Conversely, the distribution of Cr in soil showed an inverse correlation with the concentrations of Mg, Al and Fe, apart from Mn and Ca. Shehzad *et al.* also found that Cr was more likely to be adsorbed to soils with high Mn concentrations.[47] Besides, Mn oxides were proven to be the only naturally occurring oxidant of Cr(III).[48] Soil elements (*e.g.* Al, Mn and Fe) play an important role in the concentration of heavy metals in different treatments.

In addition, the combination of CA and FeCl$_3$ exhibited an obvious synergistic effect on the removal of heavy metals, especially for Cr, in different treatments (Table 2). Notably, there was no significant difference in the removal of Cd and Zn in different soil particle-size fractions (Table 2). It was illustrated that Cd and Zn in smaller soil particle sizes could be also effectively removed by CA and FeCl$_3$. However, the removal efficiencies of Cr and Pb in fine sand were lower than the other groups, which was consistent with the above results. It was elucidated that fine sand had a strong adsorption capacity for Cr and Pb.[49] In short, heavy metals in smaller soil particle-size fractions could be removed efficiently by composite washing.

3.4. Speciation of heavy metals in different soil particle-size fractions

Five chemical fractions of heavy metals were extracted by Tessier's method: exchangeable (F_1), bound to carbonates (F_2), bound to Fe–Mn oxides (F_3), bound to organic matter (F_4) and residual fractions (F_5).[50] Our results showed that the bound to carbonates (36.0–41.7%) and Fe–Mn oxides (30.4–39.2%) fractions were the main speciation options for Cd (Fig. 3A). A large amount of labile fractions ($F_1 + F_2 + F_3$, 93.4–96.2%) in the soil resulted in the high removal of Cd from the soil.[51] After remediation, most of the labile fraction of Cd in the soil was removed by CA and FeCl$_3$, and the residual fraction was predominant in the soil (54.7–60.7%). Similarly, the bound to Fe–Mn oxides (49.3–54.7%) and carbonates (37.8–46.3%) fractions were the main speciation sources for Zn (Fig. 3D), which were removed effectively by washing with CA and FeCl$_3$.

In addition, the bound to Fe–Mn oxides fraction was the main Cr speciation option (45.8–69.4%), followed by the residual fraction (Fig. 3B). Notably, a large amount of the residual fraction existed in different soil particle-size fractions, especially in fine sand (42.0%), which resulted in the lower Cr removal efficiency.[22] In addition, the bound to carbonates (31.7–

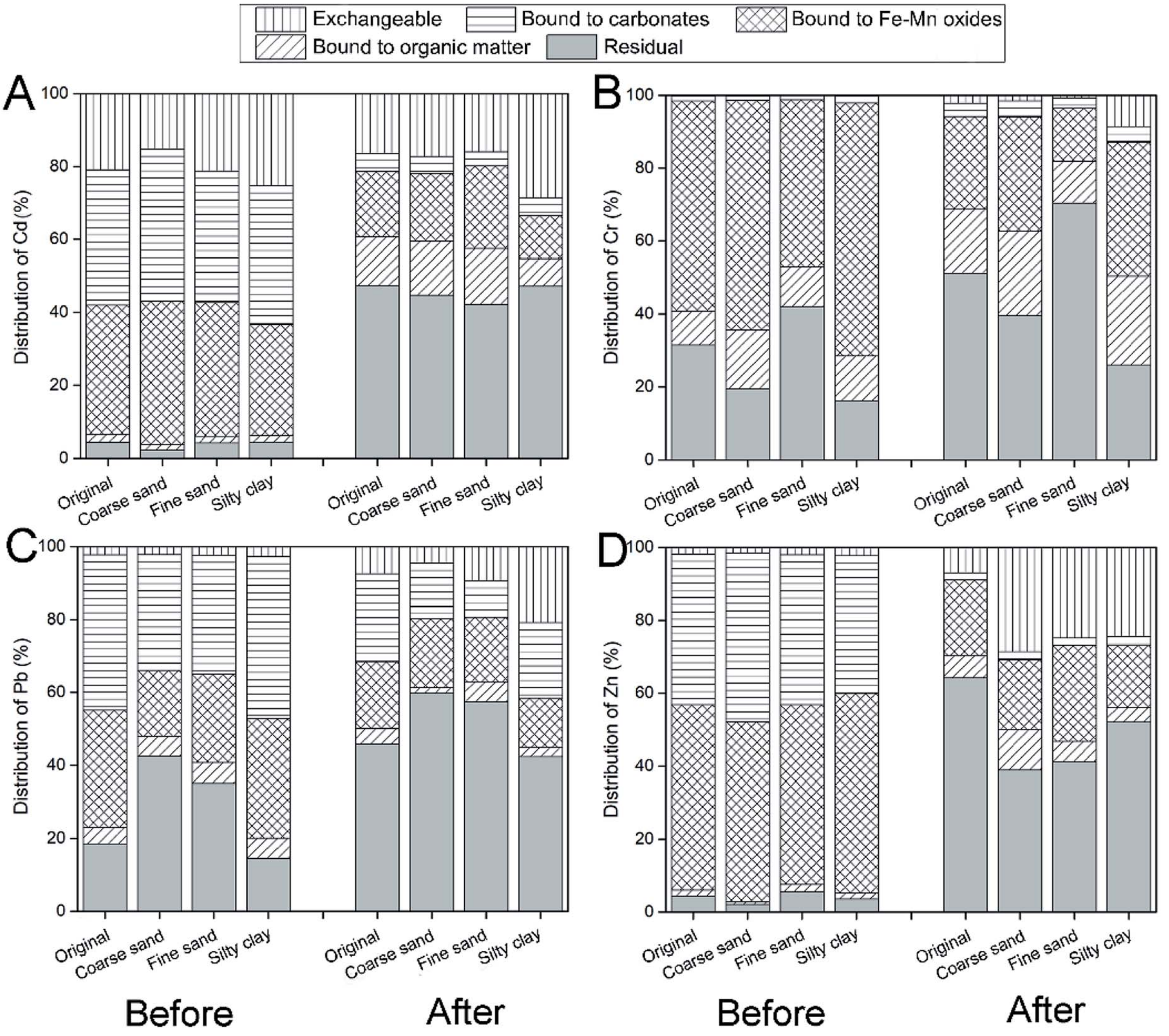

Fig. 3 The speciation of Cd (A), Cr (B), Pb (C) and Zn (D) in different particle-size fractions of soil before and after washing.

44.4%) and Fe–Mn oxides (28.1–32.7%) fractions were the main speciation source of Pb (Fig. 3C). Carbonates and Fe–Mn oxides showed a high affinity to Pb in soil, which was consistent with the previous correlation analysis and studies.[46] After washing, the labile fraction of Cr and Pb was removed significantly by CA and $FeCl_3$, and the residual fraction was the main speciation source for heavy metals.

In summary, the labile fraction ($F_1 + F_2 + F_3$) of heavy metals was removed effectively by composite washing, and residual fraction was predominant in soil after remediation. The bioavailability of Cd, Cr, Pb and Zn in soil was reduced by washing with CA and $FeCl_3$.

3.5. Risk assessment of heavy metals in soil

The geo-accumulation index (I_{geo}) was used to evaluate the pollution level of heavy metals in contaminated soil. The calculation equation for I_{geo} index is presented as follows:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right)$$

where C_n and B_n are the concentrations of heavy metals in samples and background soil, respectively. The factor 1.5 is applied as the background matrix correction value.[52] The geochemical background concentrations of Cd, Cr, Pb and Zn in soil in Hangzhou City, Zhejiang Province, China are 0.11, 79.0, 26.5 and 83.3 mg kg^{-1}, respectively.[53]

There was no significant difference in the I_{geo} index of Cd in different particle-size fractions of soil before washing (11.9–12.0) (Fig. 4A). The highest I_{geo} indexes of Cr and Pb respectively were 5.5 and 8.3 in the fine sand, which was consistent with the above results. Also, the I_{geo} index of Zn was increased with the decreasing soil particle size. The indexes of Zn in coarse sand, fine sand and silty clay were 7.0, 7.2 and 7.5, respectively. The soil was very strongly polluted by Cd, Cr, Pb and Zn ($I_{geo} \geq 5$). After composite washing, the I_{geo} index of the heavy metals was decreased in all treatments, indicating that the polluted level of heavy metals in soil was reduced by CA and $FeCl_3$. The polluted level of Cr and Zn was moderately to strongly polluted ($3 > I_{geo} \geq 2$) after remediation.

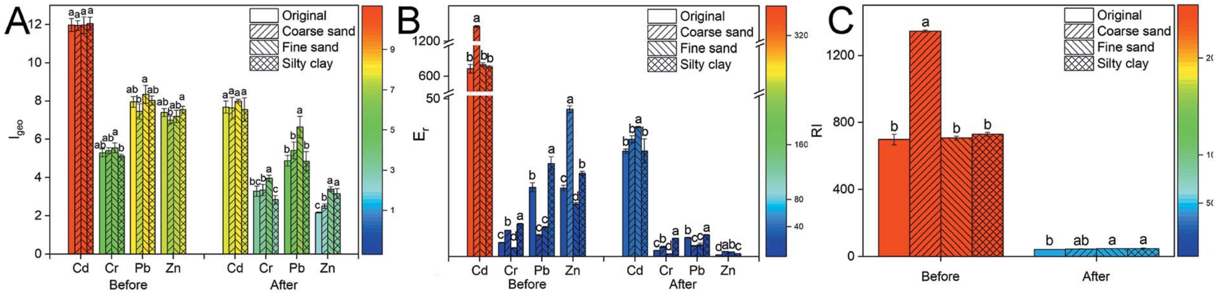

Fig. 4 The geo-accumulation index (I_{geo}) (A), ecological risk coefficient (E_r) (B) and potential ecological risk index (RI) (C) of heavy metals in soil in different treatments. Different letters (a–d) on the top of the error bars indicate a significant difference among different treatments (one-way ANOVA, $P < 0.05$).

The ecological risk coefficient (E_r) and potential ecological risk index (RI) are used for the ecological risk evaluation of heavy metals in soil.[54] The calculation equations for RI and E_r are presented as follows:

$$\mathrm{RI} = \sum_{i=1}^{n} E_r{}^i$$

$$E_r{}^i = T_r{}^i \times C_r{}^i$$

$$C_r{}^i = \left(\frac{F_1 + F_2 + F_3 + F_4}{F_5}\right)_i$$

where, $C_r{}^i$ is the contamination factor of heavy metals. F_1, F_2, F_3, F_4 and F_5 are the concentrations of heavy metals of different chemical fractions extracted by Tessier's method. F_1, exchangeable; F_2, bound to carbonates; F_3, bound to Fe–Mn oxides; F_4, bound to organic matter; F_5, residual. $T_r{}^i$ is the toxicity coefficient of heavy metals (Cd(30), Cr(2), Pb(5), and Zn(1)).[55]

Before washing, the ecological risk coefficient (E_r) of Cd (Fig. 4B) was extremely high in the coarse sand, which was related to the higher labile fractions of Cd in soil. The risk level of soil polluted by Cd was very high ($E_r \geq 320$) in all treatments. Similarly, the risk level of soil polluted by Zn was medium ($80 > E_r \geq 40$) in coarse sand, which was higher than that in the other groups. Although the I_{geo} index of heavy metals showed that the soil was very strongly polluted by Cr and Pb, the potential

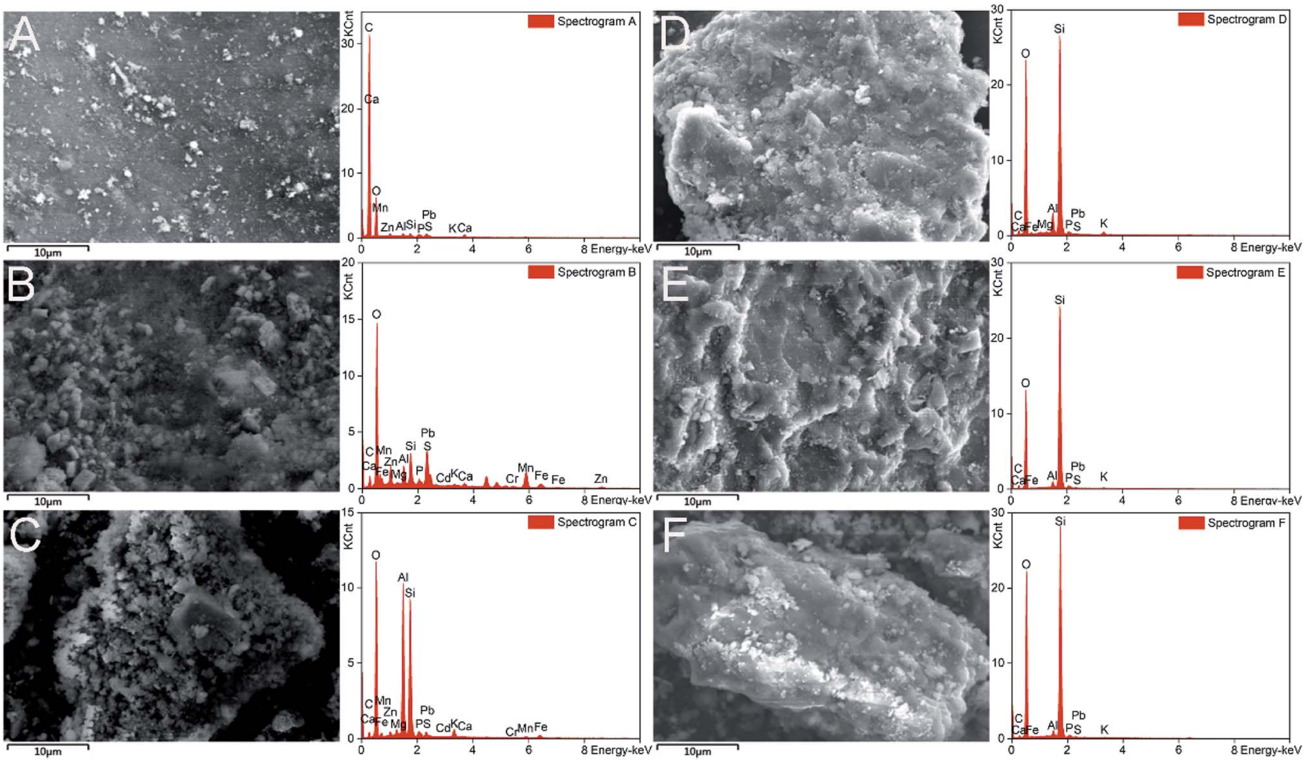

Fig. 5 SEM and EDS images of soil before (A–C) and after (D–F) washing. A(D), B(E), and C(F) are images of the coarse sand, fine sand and silty clay, respectively.

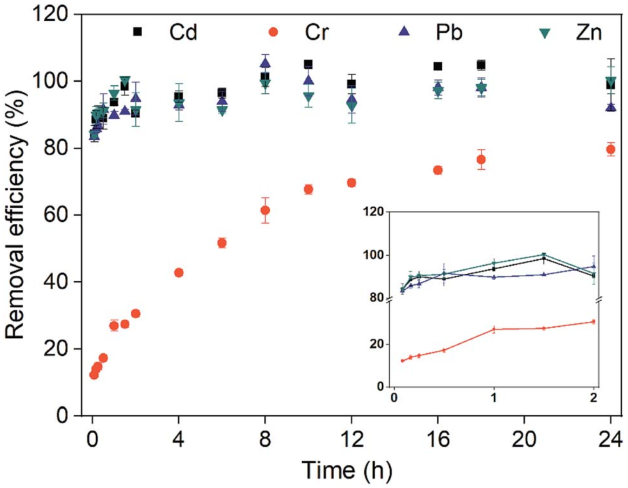

Fig. 6 Removal efficiencies of Cd, Cr, Pb and Zn in contaminated soil by washing with CA and $FeCl_3$ in the slurry reactor system; the removal efficiencies of Cd, Cr, Pb and Zn at the first 2 hours (the inset graphic).

ecological risk level was low ($40 > E_r$). After washing with CA and $FeCl_3$, the potential ecological risk of soil polluted by heavy metals was reduced from an extremely high level ($RI \geq 600$) to a low level ($150 > RI$) (Fig. 4C).

3.6. Surface morphology of soil particles

The surface morphology and elemental distribution of soil particles were further explored by SEM-EDS. Micro-aggregates were found on the soil surface, especially on the fine sand and silty clay (Fig. 5B and C), which may contribute to the adsorption of heavy metals.[49] No micro-aggregates were observed and the soil surface became smoother after washing with CA and $FeCl_3$ (Fig. 5D–F). It could be inferred that the removal of heavy metals was related to the disappearance of those micro-aggregates.[56]

The EDS analysis showed that O, Si, Al and C were predominant elements in the soil (Fig. 5). The contents of elements (*e.g.* Al, Mn and Fe) in the soil were decreased after washing. In addition, FTIR analysis was used to identify the functional groups of the soil.[57] Hydroxyl and carboxyl groups were proven to be important in the adsorption of heavy metals in soil.[58] In this study, the disappearance of carboxylic groups (1427 cm^{-1}) and hydroxyl groups (1036 cm^{-1}) illustrated the dissolution of organic matter after washing (Fig. S5†). These results revealed that soil elements (*e.g.* Al, Mn and Fe) and organic matter were dissolved by CA and $FeCl_3$, which promoted the desorption of heavy metals from the soil.

3.7. Removal of heavy metals in a slurry reactor

In the lab, most of the experiments were small-scale washing tests in centrifuge tubes.[3,59,60] Subsequently, large-scale stirring and washing equipment were used.[61,62] Here, the removal of heavy metals in a slurry reactor was investigated to explore the application of washing with CA and $FeCl_3$. After washing, the soil organic matter content decreased from 8.7% to 7.7%, and the pH decreased from 7.0 to 3.5. It was illustrated that acidification was one of the important mechanisms for the removal of heavy metals. Meanwhile, most of the Cd, Pb and Zn in the soil (>90%) were removed within 1.5 h (Fig. 6). Conversely, only 27.4% of Cr was removed from the soil after washing for 1.5 h. Then, the desorption of heavy metals achieved a dynamic equilibrium gradually. Finally, the removal efficiencies of Cd, Cr, Pb and Zn increased slowly and reached 94.8%, 79.5%, 92.7% and 97.2%, respectively.

After remediation, the concentrations of Cd, Pb and Zn in the soil were 33.8, 700.2 and 559.3 mg kg^{-1}, which were lower than the risk screening values in the environmental protection administration guidelines of China.[63] Additionally, the Cr(VI) concentration in soil (65.2 mg kg^{-1}) was lower than the risk intervention value in the environmental protection administration guidelines of China.[63] It was determined that column washing with CA and $FeCl_3$ could be used at full scale.

4. Conclusions

In conclusion, CA and $FeCl_3$ were selected from 7 washing agents for co-contaminated soil remediation. The optimum washing conditions were determined to be: CA (0.86 mol L^{-1}), $FeCl_3$ (1.00 mol L^{-1}), washing time (10 h) and liquid : soil ratio (10 : 1). Heavy metals in smaller-size soil particles could be efficiently removed by washing. The bioavailability of heavy metals in soil was decreased after washing. The potential ecological risk of heavy metals in different treatments was reduced from an extremely high level to a low level. Furthermore, soil elements (*e.g.* Al, Mn and Fe) and organic matter were dissolved by CA and $FeCl_3$, which promoted the desorption of heavy metals from the soil. In addition, washing with CA and $FeCl_3$ could be used at full scale, resulting in the effective reduction of health risks from heavy metals in soil after washing.

Conflicts of interest

There are no conflicts to declare.

Abbreviations

CA	Citric acid
OA	Oxalic acid
$FeCl_3$	Ferric chloride

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